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TECHNICAL NOTE
Crystallinity of Recycled PET Fibers from Chemical and Mechanical Reprocessing

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ABSTRACT: This work investigated the effect of isophthalate (iso) content in poly(ethylene terephthalate) (PET) materials on its degree of crystallinity (χ%) and mechanical properties. Melt blends were prepared from virgin (0 iso-wt.%) and bottle-grade (1.7 iso-wt.%) PET and subsequently spun into fibers. The mechanical and crystallinity properties were determined using differential scanning calorimetry (DSC), X-ray diffraction (XRD), and uniaxial tensile testing. The crystallinity results determined from DSC and XRD quantified the relationship between iso-content and χ% in the materials. It was found that melt-mixing of different isophthalate grades had a lesser effect on melting temperature (T_m) and χ% than chemically recycled random copolymers of terephthalate and isophthalate. It was further shown that random copolymers of $<$0.25 iso-wt.% had comparable crystallinity to the virgin high-modulus low-shrink (HMLS) materials.

KEY WORDS: recycling, PET fibers, isophthalate removal, tire cord, crystallinity

Introduction

High strength poly(ethylene terephthalate) (PET) tire cords require high degrees of crystallinity in order to meet the mechanical properties for reinforcement [1]. Manufacturing PET tire cords from recycled polyester bottles is an emerging approach for reducing the consumption of raw materials and carbon footprint of the tire industry. However, PET bottles have their own set of requirements such as clarity and low intrinsic viscosity (IV) for blow molding of preforms [2,3]. These parameters are met through introducing a small quantity (approximately 2.0 iso-wt.%) of isophthalate comonomer (Fig. 1), which disrupts the chain-packing during crystallization [4]. It is therefore challenging to directly use post-consumer recycled PET in tire cord applications as a result of this decreased crystallinity and lower modulus. Furthermore, there exists differences between the feedstock purity from mechanical (i.e., melt-blending) and chemical (i.e., depolymerization) recycling methods. Herein, we quantify the effects of isophthalate content (iso-wt.%) on the crystallinity and tensile modulus and identify the isophthalate tolerance (0.2 iso-wt.%, detailed below) in which recycled, bottle-grade PET is comparable to virgin HMLS PET.

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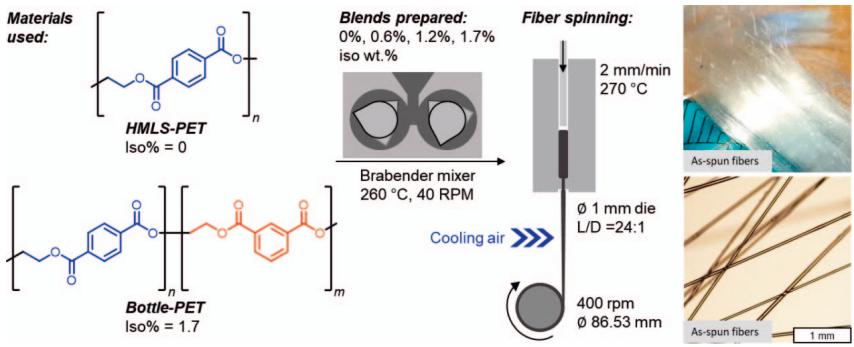

FIG. 1 — *Preparation process of PET fibers with different amounts of isophthalate via melt blending.*

Recycled PET Copolymers

Two approaches to obtain various isophthalate contents (iso-wt.%) of PET materials were compared in this work. First, melt-blending of HMLS PET and bottle grade PET materials in a Brabender Plasticorder mixer produced PET mixtures with various weight percentages of isophthalate. The isophthalate content was quantified using ^{1}H NMR integrations in $CDCl_3$ with 10 vol.% deuterated trifluoroacetic acid. Fibers were spun using a plunger speed of 2 mm/min at 270 °C through a 1 mm die of a length/diameter ratio of 24:1 and collected with air cooling on a bobbin spun at 400 rpm using a motor. The fiber materials were then annealed at 130 °C for 10 min before testing. The second approach was a copolymerization of bis(2-hydroxyethyl) terephthalate with bis(2-hydroxyethyl) isophthalate through Sb_2O_3 (0.02 mol%) catalyzed copolymerization at 270 °C under reduced atmosphere (30 Pa) for 8 h. Samples were then solid-state polymerized (SSP) at 230 °C to further increase the degrees of polymerization (DP_n). In this study, the mechanical properties and crystallinity were studied in the melt-blended samples, whereas only crystallinity measurements were made for the random copolymers due to their lower intrinsic viscosities after SSP which made fiber spinning difficult.

Crystallinity Measurements

Blends of bottle and HMLS PETs were first studied by DSC. The sample with 0 iso-wt.% had a melting temperature (T_m) of 255.0 °C, while the 1.7 iso-wt.% exhibited a T_m of 251.3 °C (Fig. 2). The enthalpy of fusions ranged from 49.0 to 46.2 J/g, corresponding to a degree of crystallinity of 34.8 and 32.7%, respectively (Fig. 2).

By comparison, the random copolymer of poly(ethylene terephthalate-co-ethylene isophthalate) had melting points ranging between 246–254 °C at 1.6

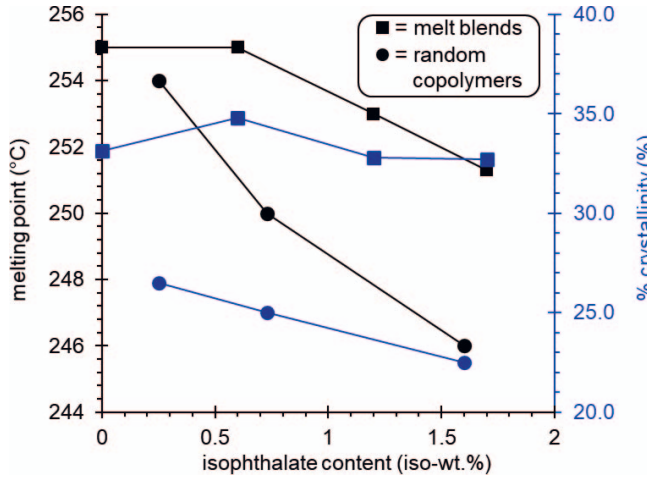

FIG. 2 — *Melting temperature and crystallinity of blends and random copolymers.*

and 0.25 iso-wt.%, respectively. The enthalpies of fusion were 37.1 and 31.5 J/g corresponding to a degree of crystallinity of 26.5 and 22.5%, respectively (Fig. 2). The structure of melt-blended material was likely a combination of the two PET polymer grades or a block copolymer of pure terephthalate blocks and isophthalate containing blocks, while the synthesized random copolymers were expected to have uniform isophthalate distribution. We attribute the differences observed from mechanically recycled PET and chemically recycled PET crystallinity to these differences. The uniform distribution of comonomers prevents packing of more crystal unit cells and in turn lowers the degree of crystallinity compared to melt-blended materials (Table 1) [5].

Mechanical Measurements

Elastic modulus of PET blends in the form of single fibers were obtained from stress-strain curve analysis. Despite a large standard deviation, the Young's modulus of technical grade PET (0 iso-wt.%) was found to be 22.6 ± 6.2 MPa, 25% greater than the 1.7 iso-wt.% samples (18.1 ± 0.8 MPa). A monotonic reduction of Young's modulus with increased isophthalate incorporation is seen in Fig. 3. This observation confirmed that the mechanical strength has strong correlation with the isophthalate content in the blend materials. In this context, a lower comonomer concentration produces greater strength.

As for the random copolymer, the tensile property assessment was not possible. Additional investigation is needed to determine the effect of isophthalate content on mechanical properties. This will provide enhanced

TABLE 1 — *Materials used and synthesized for crystallinity studies.*

Entry (no.)	PET source (grade)[a]	Degree of polymerization (DP_n)[b]	Isophthalate (iso-wt.%)[b]	T_m (°C)[c]	ΔH (J/g)[c]	Crystallinity (χ%)[d]
1	HMLS	416	0.00	255	46.4	33.1
2	65:35 blend	422	0.60	255	48.7	34.8
3	30:70 blend	426	1.20	253	45.9	32.8
4	bottle	430	1.70	251	45.8	32.7
5	random	102	0.25	254	37.1	26.5
6	random	175	0.73	250	35.0	25.0
7	random	129	1.60	246	31.5	22.5

[a]HMLS grade PET was provided by Pirelli, bottle grade PET was collected from discarded Kirkland water bottle, and random copolymers were prepared from polycondensation polymerization of the respective ethylene glycol phthalate esters.
[b]Degree of polymerization and isophthalate incorporation measured by ^{1}H NMR analysis in $CDCl_3$:TFA (8:1).
[c]Measured by peak temperature and integrated heat flows in differential scanning calorimetry (DSC) at a heating rate of 10 °C/min.
[d]Determined as the quotient of $\Delta H/\Delta H^0$(PET), where ΔH^0(PET) = 140 J/g [6].

confidence in the comonomer tolerance in chemically recycled PET for the purpose of reuse in tire cords.

Conclusions

From these findings, we can draw conclusions regarding the melting temperatures and % crystallinities of the copolymers and their tolerance as recycled feedstocks. Melt-blended samples from mechanical recycling affords PET materials with little changes in the range of 0–1.7 iso-wt.% ($\chi\%_{avg} = 33.35$

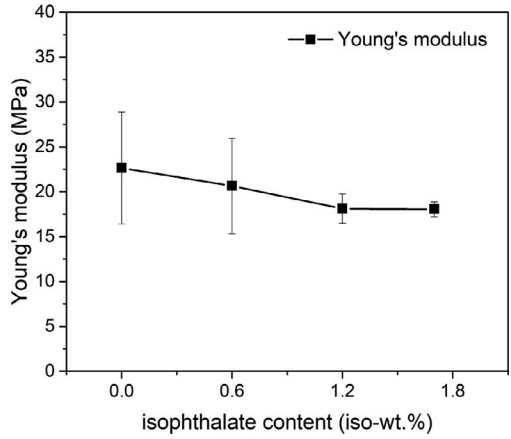

FIG. 3 — *The Young's modulus of annealed PET fibers prepared from melt blending.*

$\pm$ 0.98%), whereas random copolymers were more affected by iso-wt.% ($\chi\%_{avg}$ = 24.70 $\pm$ 2.02%). Both recycling processes exhibit T_m dependance on iso-wt.%, but at different tolerances. The melt-blended samples at 0.6 iso-wt.% have approximately the same thermal properties as the HMLS grade PET, but T_m decreases beyond this loading, down to 251.3 °C at 1.7 iso-wt.%. The chemically recycled random copolymer samples at 0.25 iso-wt.% have approximately the same T_m (254.0 °C) as HMLS grade PET, but the $\chi\%$ is depressed at 26.5%. We conclude that mechanically recycled blends may tolerate 0.6 iso-wt.%, corresponding to a 65:35 wt. ratio of HMLS: bottle PET; and that chemically recycled random copolymers may have a lower tolerance of 0.25 iso-wt.%. It is therefore of significance that recycled PET fibers for tire-cord application are properly purified according to their recycling methods. It was also confirmed that mechanical properties of spun fibers reduced with an increase of isophthalate content. Enhanced methods of purifying isophthalate containing copolymers are under active development and may provide the advantages in the reutilization of plastic bottles for tire cord applications.

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